

# Considerations from the past for the future of mineral carbonation

Prof. Rafael M. Santos

University of Guelph, Guelph, Ontario, Canada

MSc. Pol Knops

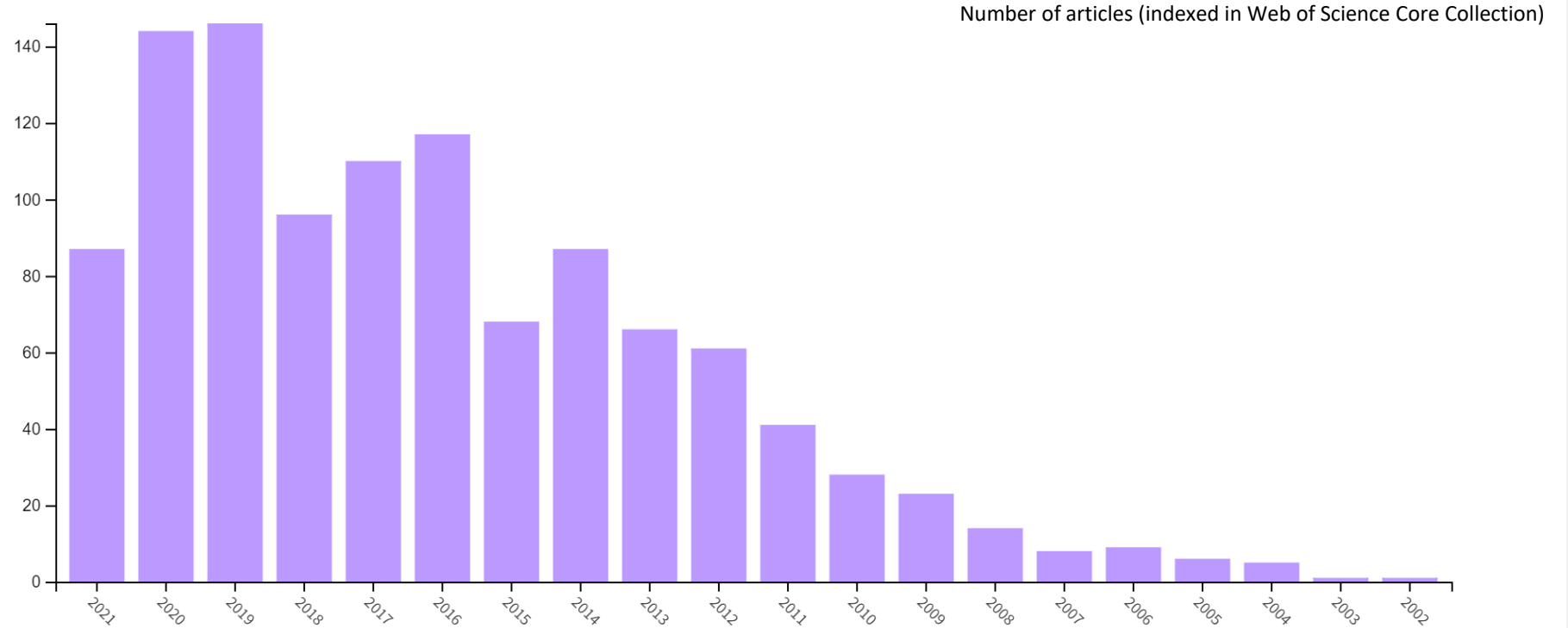
Green Minerals, Twello, The Netherlands

UNIVERSITY  
of GUELPH

IMPROVE LIFE.

ARPA- E Workshop: SCHEMA (Sequestering Carbon  
with Hybrid Employment of Mineral Assets)  
July 15<sup>th</sup> 2021

# Bibliometric Trends (1)



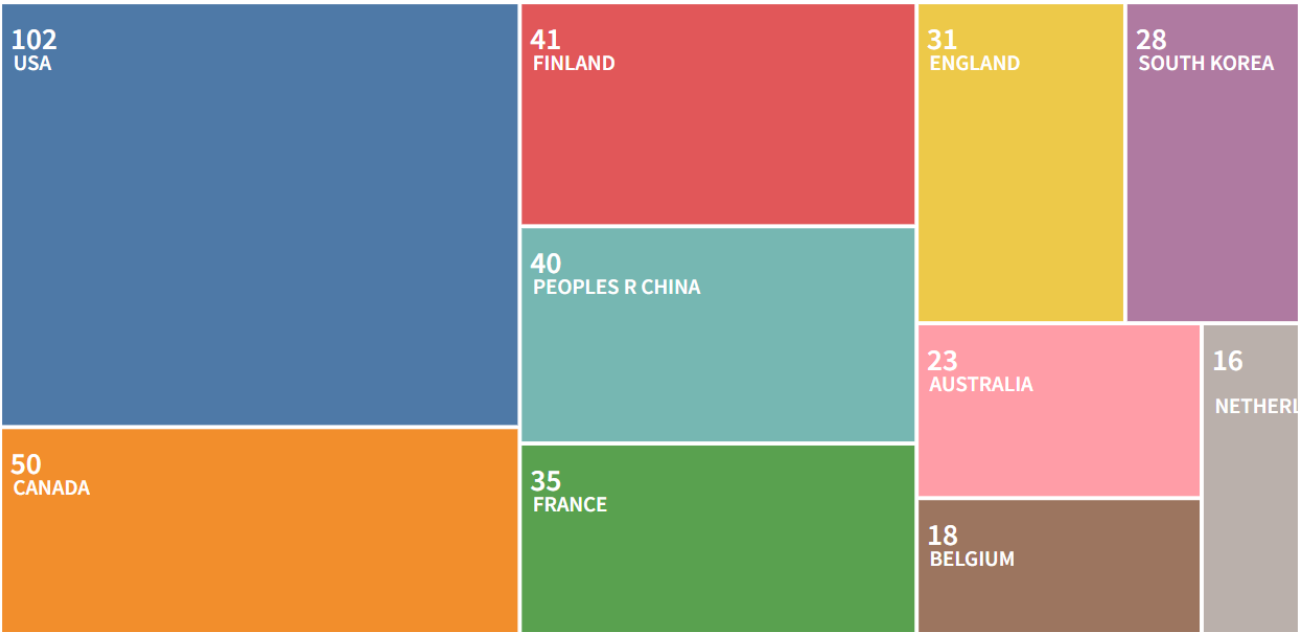
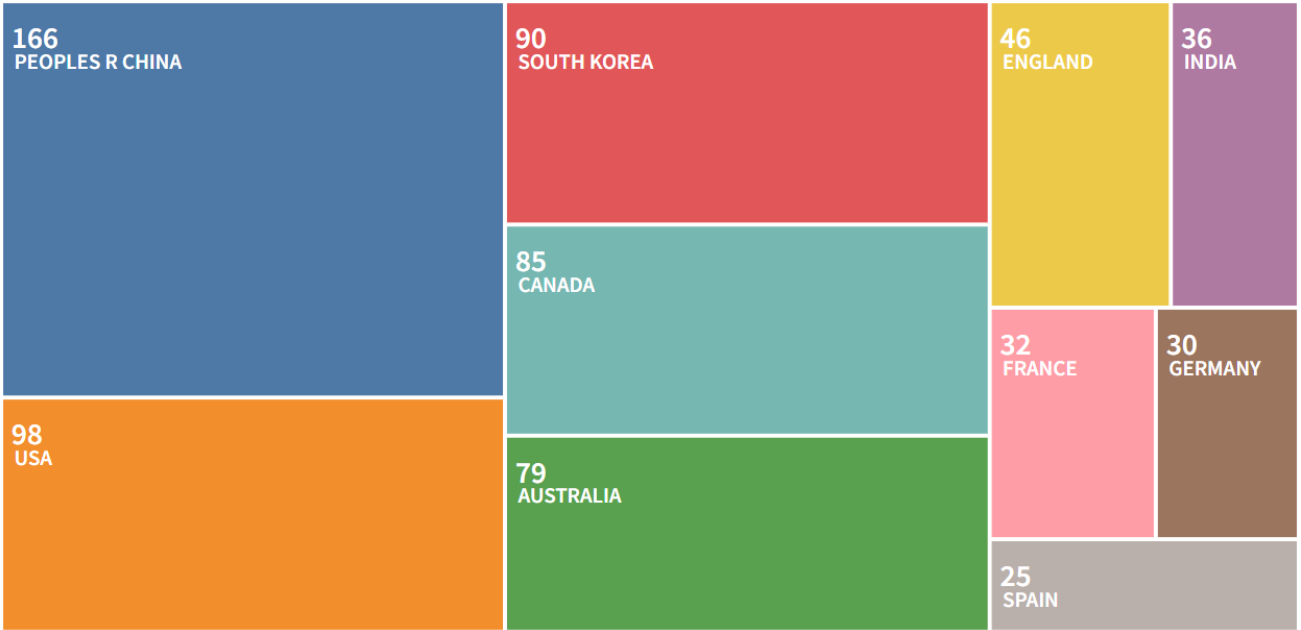
TOPIC: ("mineral carbonation" OR "CO2 minerali\*" OR "mineral carbon sequestration")

# Bibliometric Trends (2)

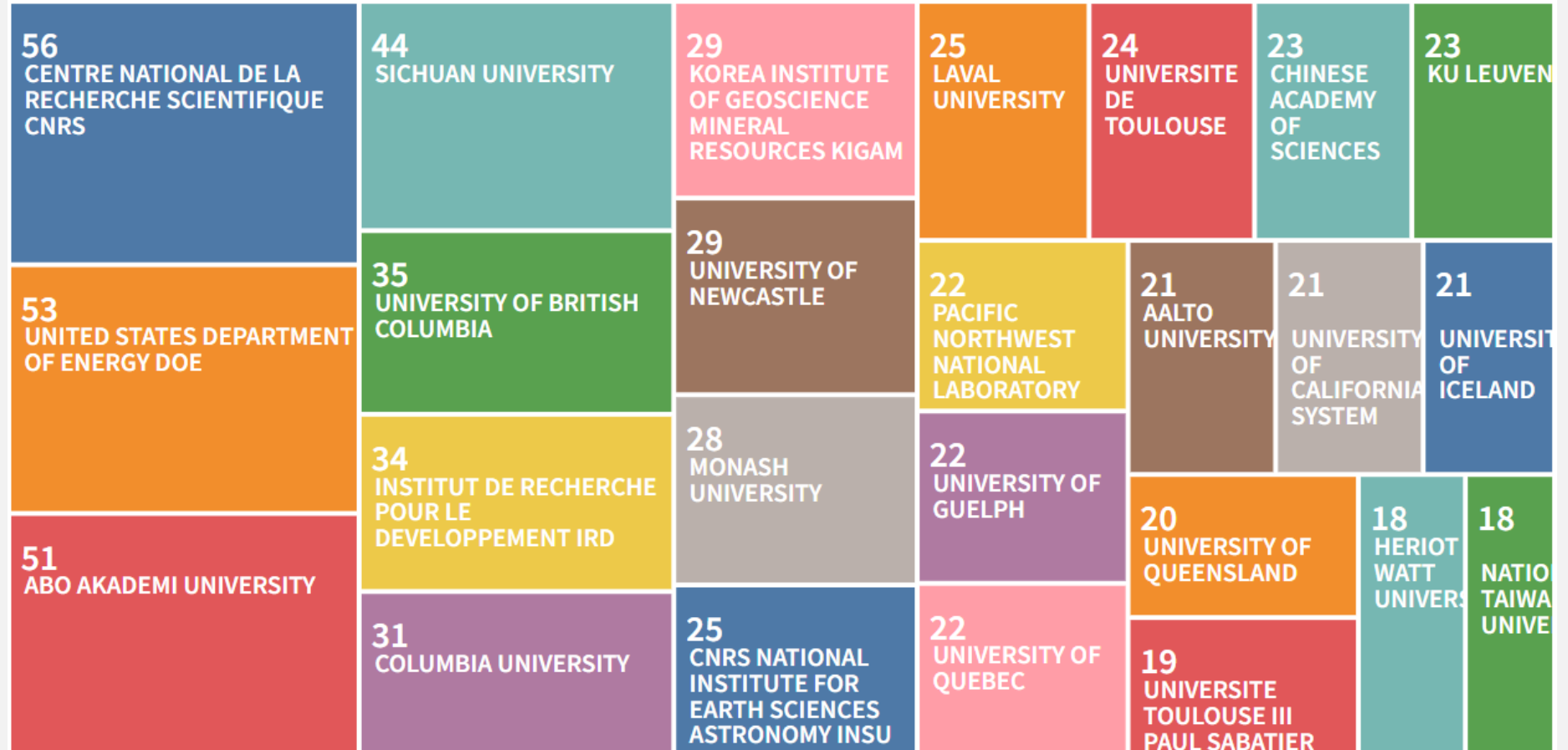
TOPIC: ("mineral carbonation" OR "CO2 minerali\*" OR "mineral carbon sequestration")

2016-2021:

2002-2015:



## Bibliometric Trends (3)



TOPIC: ("mineral carbonation" OR "CO2 minerali\*" OR "mineral carbon sequestration")

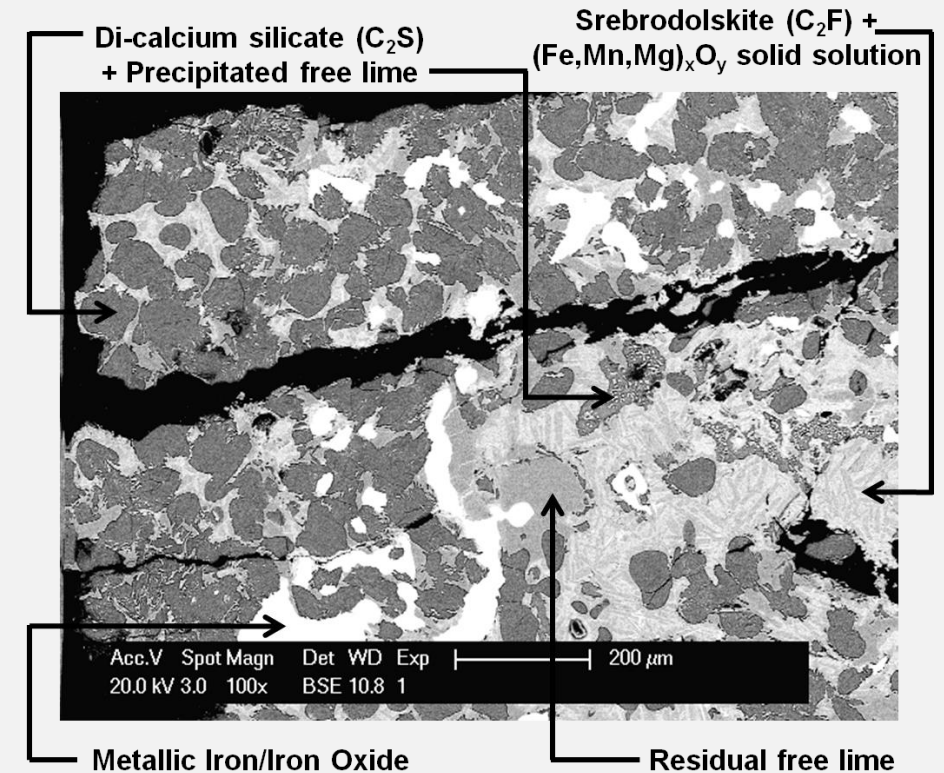
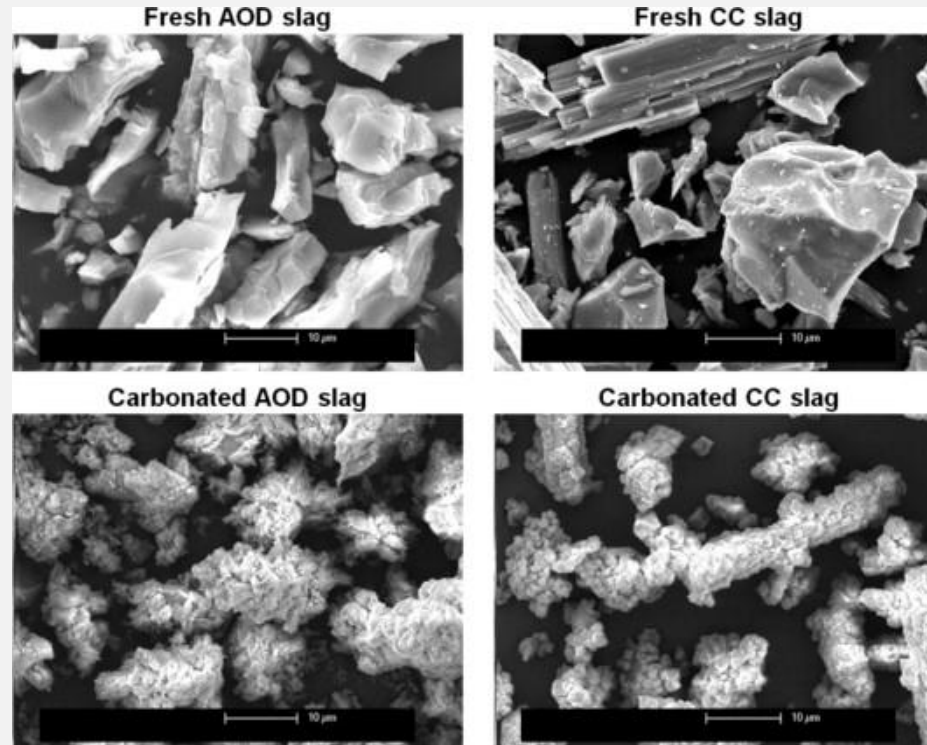
# Periodic Table of Carbonates

H <sub>2</sub> CO <sub>3</sub>																He	
Li <sub>2</sub> CO <sub>3</sub>	BeCO <sub>3</sub>											B	C	N	O	F	Ne
Na <sub>2</sub> CO <sub>3</sub>	MgCO <sub>3</sub>											Al <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub>	Si	P	S	Cl	Ar
K <sub>2</sub> CO <sub>3</sub>	CaCO <sub>3</sub>	Sc	Ti	V	Cr	MnCO <sub>3</sub>	FeCO <sub>3</sub>	CoCO <sub>3</sub>	NiCO <sub>3</sub>	CuCO <sub>3</sub>	ZnCO <sub>3</sub>	Ga	Ge	As	Se	Br	Kr
Rb <sub>2</sub> CO <sub>3</sub>	SrCO <sub>3</sub>	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag <sub>2</sub> CO <sub>3</sub>	CdCO <sub>3</sub>	In	Sn	Sb	Te	I	Xe
Cs <sub>2</sub> CO <sub>3</sub>	BaCO <sub>3</sub>		Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl <sub>2</sub> CO <sub>3</sub>	PbCO <sub>3</sub>	Bi	Po	At	Rn
Fr	Ra		Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Uut	Uuq	Uup	Uuh	Uus	Uuo



La <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub>	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

# Particle exterior versus interior (1)

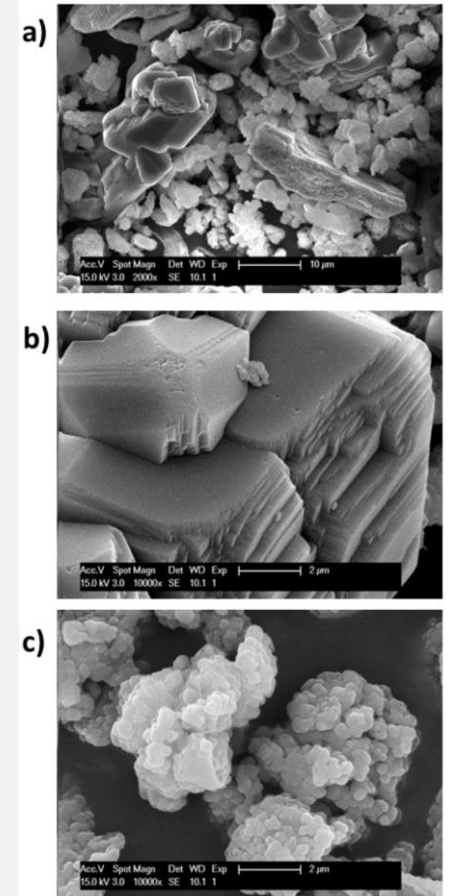
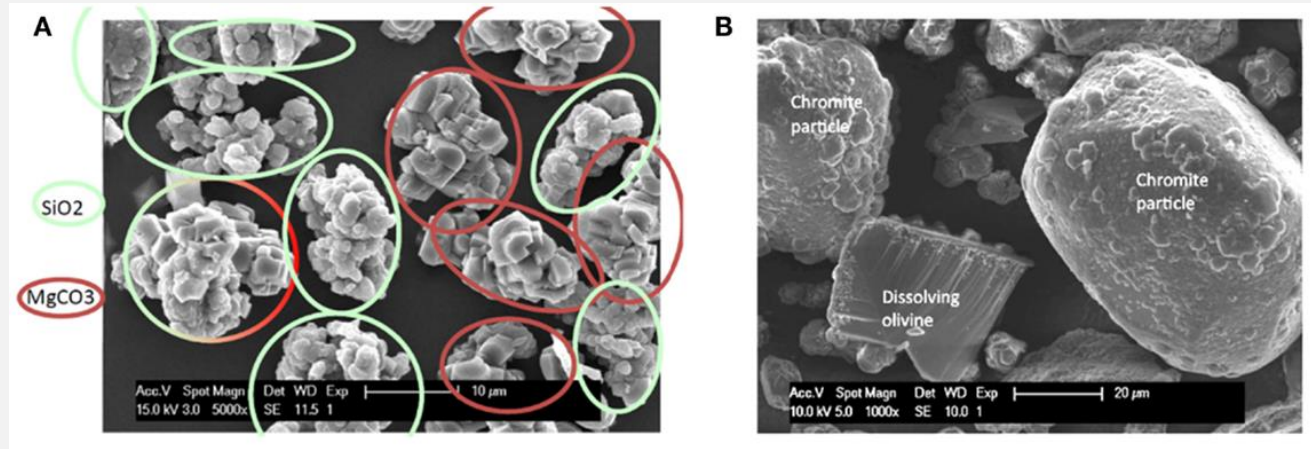


UNIVERSITY  
of GUELPH

Stabilization of basic oxygen furnace slag by hot-stage carbonation treatment. [Chemical Engineering Journal, \(2012\), 203, 239-250.](#)

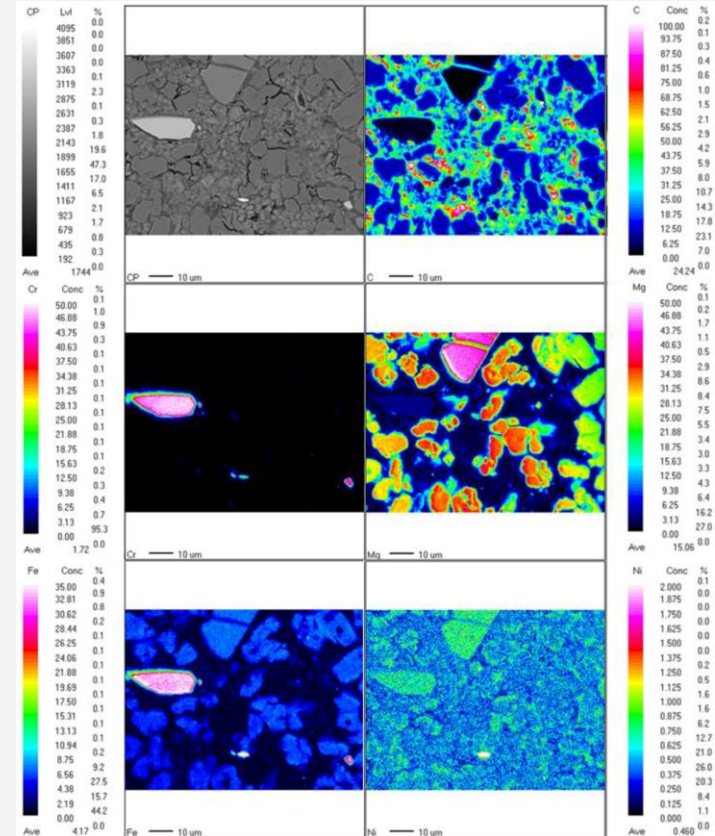
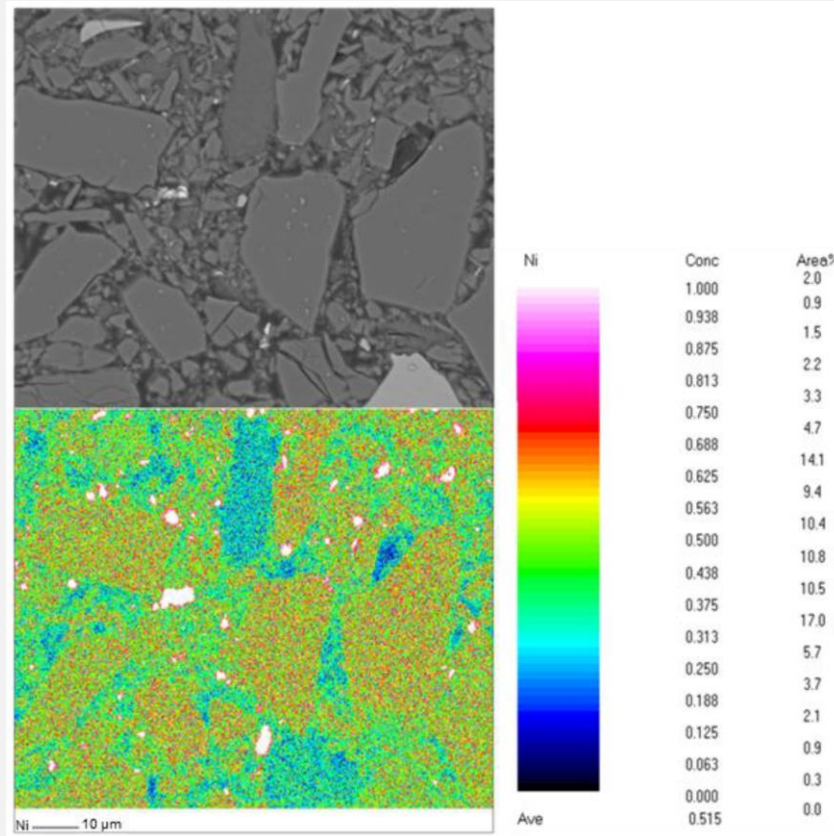
Accelerated mineral carbonation of stainless steel slags for  $CO_2$  storage and waste valorization: effect of process parameters on geochemical properties. [International Journal of Greenhouse Gas Control, \(2013\), 17, 32-45.](#)

## Particle exterior versus interior (2)



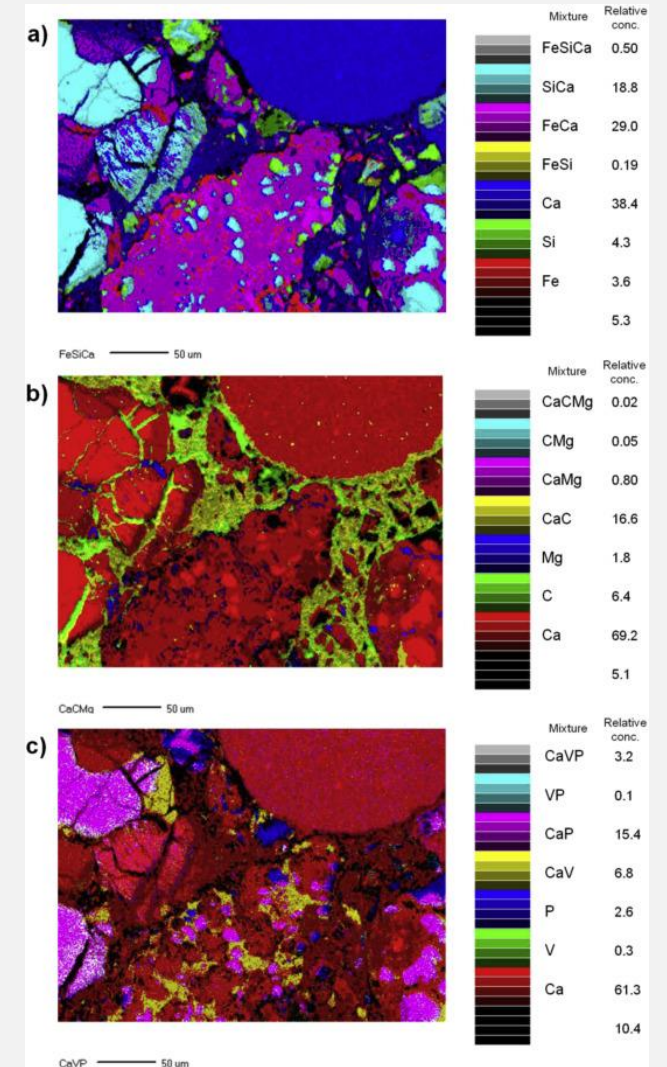
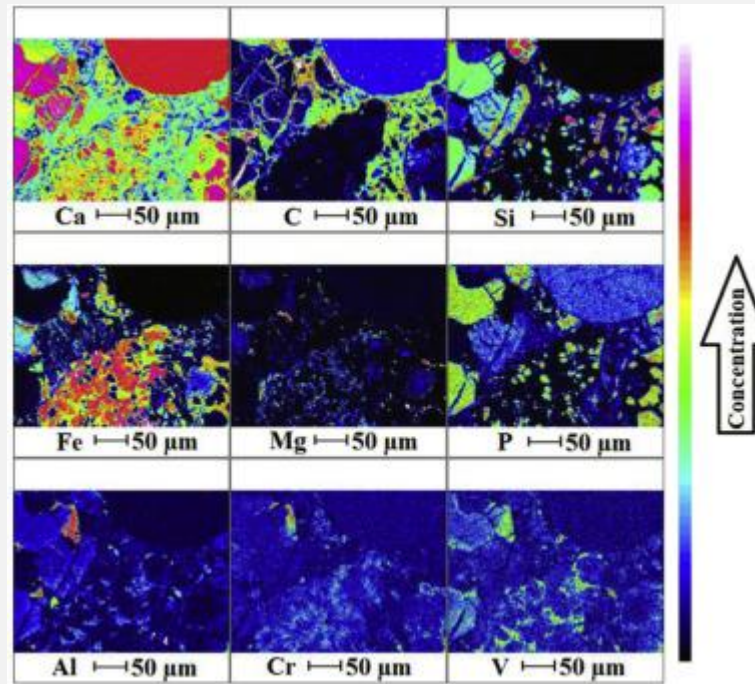
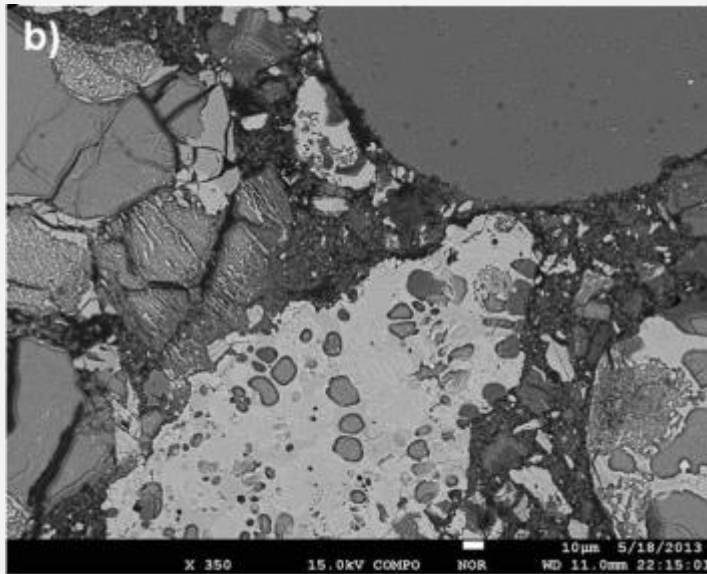


# Particle exterior versus interior (3)





# Particle exterior versus interior (4)



UNIVERSITY  
of GUELPH

Laboratory investigation of carbonated BOF slag used as partial replacement of natural aggregate in cement mortars.  
[Cement and Concrete Composites, \(2016\), 65, 55-66.](#)

# Particle Size vs. Particle Size Distribution

$$CWR = \frac{t_{carb}}{\tau_{react}} = \frac{r_x \cdot (1 - \sqrt[3]{1 - C\%/100\%})}{\tau_{react}}$$

$$\%carb = \begin{cases} \text{if } [r_x \leq t_{carb}], = 100\% \\ \text{if } [r_x > t_{carb}], = \frac{\frac{4}{3}\pi r_x^3 - \frac{4}{3}\pi(r_x - t_{carb})^3}{\frac{4}{3}\pi r_x^3} \end{cases}$$

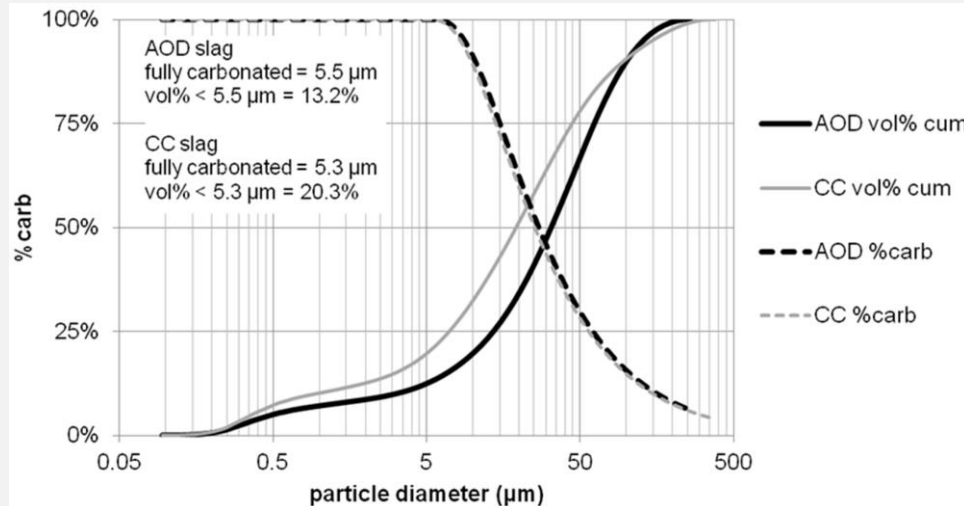
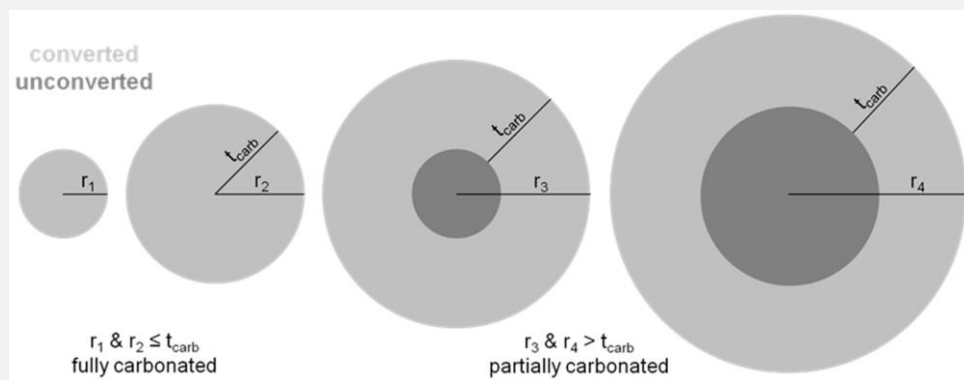
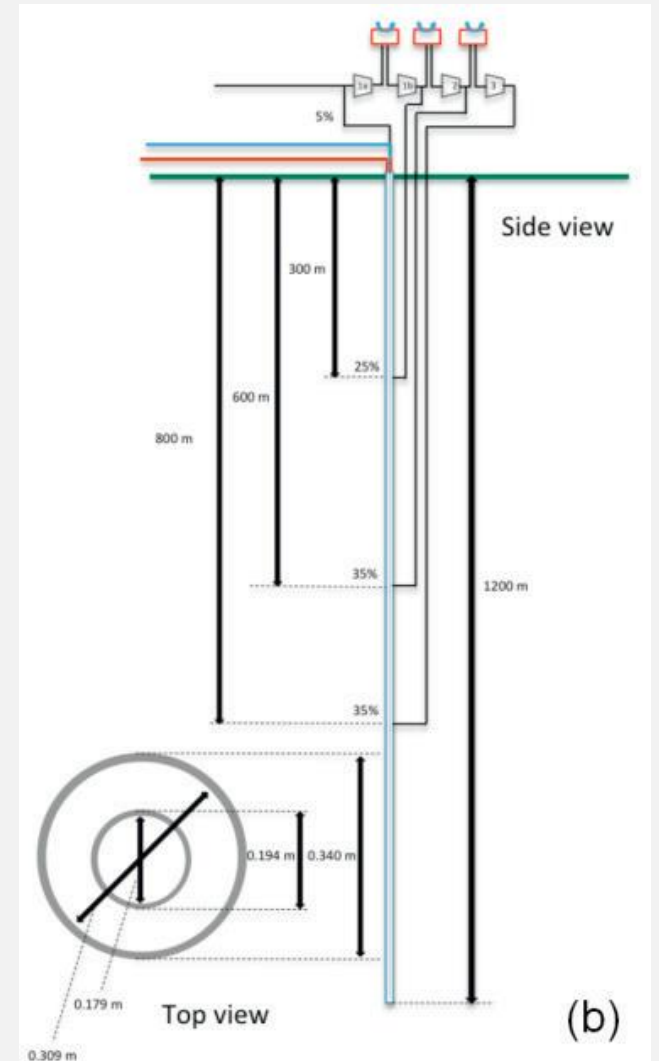
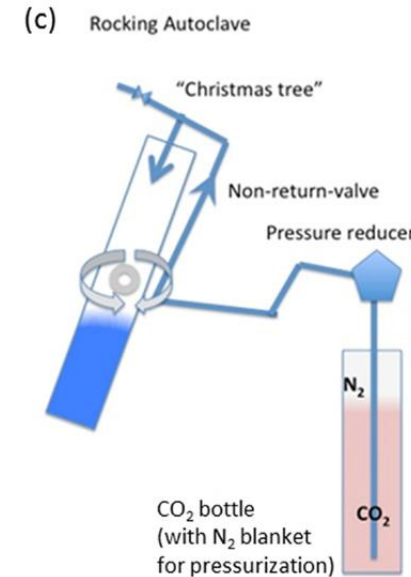
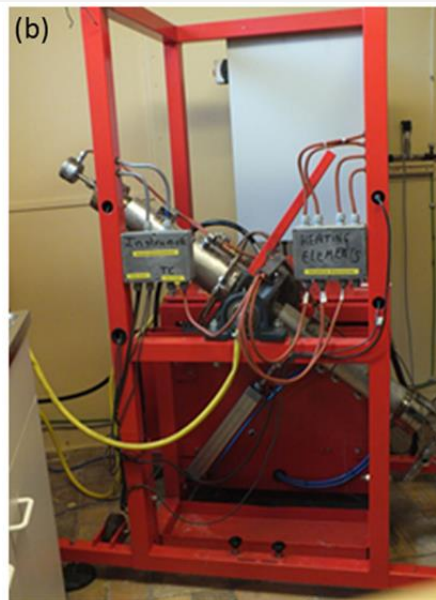
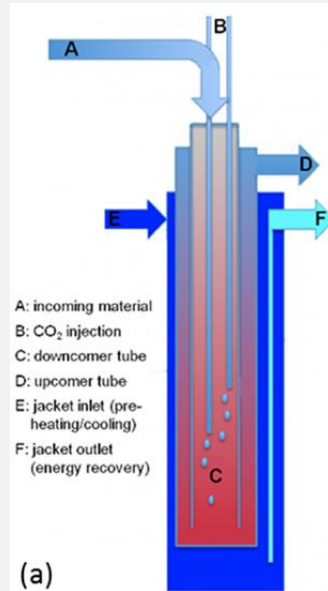


Table 3. Summary of particle size determination methods and utilization from different carbonation studies reviewed by Georgakopoulos et al. [16].

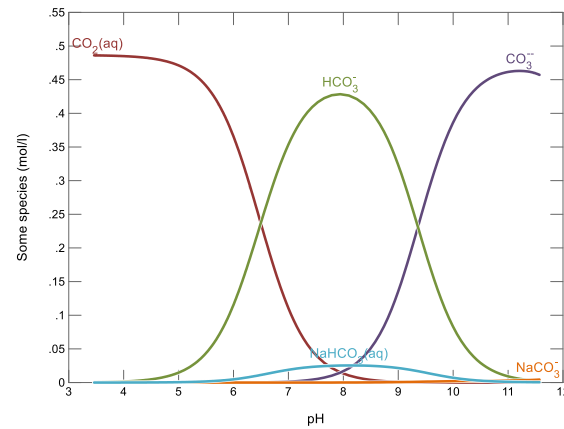
Type of Slag	Method of Particle Size Determination	How Particle Size/PSD Data Were Used
Huigen et al. [28]	Sieving was used for particle size classification; ground slag was sieved into fractions: <125 μm, <150 μm, <200 μm, <400 μm, <600 μm, <800 μm, <1000 μm. Particle size distribution and volume-based mean particle size (D4,3) and d(0.5) of samples were measured, pre-carbonation, by laser diffraction (Malvern Mastersizer 2000) using ethanol (96%) as a dispersing agent.	It was noticed from PSD that all sample fractions had wide size distribution and all included very small particles <1 μm. It was suggested that since slag particles are non-porous, the specific surface area can be estimated using the D(4,3) value, rather than performing BET analysis. Carbonation conversion was inversely proportional to particle size, and it was found that the D(4,3) value can be fitted to the conversion data to yield a predictive exponential relationship.
Cheng et al. [28]	Sieving was used for particle size classification; ground slag was sieved, with only materials passing a 44 μm mesh being used. SEM imaging was used, post-carbonation, to visualize particle size and shape.	SEM imaging qualitatively showed that particles shrank after carbonation, and that cubic particles of approximately 1–2 μm size, thought to be calcium carbonate, adhered to the surface of the remnants of slag particles. This was used as a sign that shrinking core model, with a protective carbonate layer around reacting particles, can describe the slag carbonation mechanism. The particle size (i.e., sieve mesh size) was used in a kinetic modeling equation fitted to the experimental data.
van Zonneveld et al. [27]	Sieving was used for particle size classification; slag was air-cooled, broken and sieved to obtain the particle size distribution in the range of 0–3.5 mm. Samples of 4 mm size were sieved, to <108 μm, before TGA analysis.	The size range of the pre-carbonation sieved slags corresponded to the size desired for aggregation, the intended application of carbonation. No discussion is made relating the particle size to experimental results.
Blackbitch et al. [28]	Sieving was used for particle size classification; slag was either directly sieved to <125 μm, or ball-milled followed by <125 μm.	No discussion is made relating to the particle size. Particle size, before and after grinding, appears in an equation to calculate the energy requirement to sequester one tonne of CO <sub>2</sub> .
Cheng et al. [28]	Sieving was used for particle size classification; dried slag was sieved to <45 μm. The particle size distribution of the slag, pre-carbonation, in tap water was obtained by laser diffraction (Malvern, Hydro 2000 SL10), which was adapted from the ISO 13320-1 method, with a range of 0.02–2000 μm. SEM imaging was used, post-carbonation, to visualize particle size and shape.	The value of the average particle size, determined from the PSD, was reported and compared to other studies. Particle size appears in an equation to model the reaction kinetics according to shrinking core model. SEM images showed small crystals of CaCO <sub>3</sub> on the surface of the reacting slag particles.
Cheng et al. [28]	Sieving was used for particle size classification; dried slag was sieved to <44 μm. The particle size distribution of the slag, pre-carbonation, in tap water was obtained by laser diffraction (Malvern, Hydro 2000 SL10), which was adapted from the ISO 13320-1 method, with a range of 0.02–2000 μm. SEM imaging was used, post-carbonation, to visualize particle size and shape.	The value of the average particle size, determined from the PSD, was only reported. SEM images showed small crystals of CaCO <sub>3</sub> on the surface of the reacting slag particles.
Pudovkin et al. [31]	The slag was separated through dry sieving into various size classes, but only the 83–100 μm size class was investigated.	The choice of particle size fraction used was based on previous work, where the fraction chosen exhibited the highest carbonation yield.
Blackbitch et al. [28]	Sieving was used for particle size classification; 0.425–2 mm (class A), 0.105–0.177 mm (class B), 0.105–0.177 mm (class C), < 0.105 mm (class D). Particle size distribution was determined, pre-carbonation, according to ASTM C136 standard procedure (last revised, January 2015). The distribution of particle sizes larger than 75 μm (related to the no. 200 sieve) was to be determined by sieving, while the distribution of particle sizes smaller than 75 μm was to be determined by a sedimentation process, using a hydrometer.	The particle size distribution curve indicated that the slag could be classified as sandy granular material. Loss on ignition (LOI) was performed on each size fraction, and it was found that finer fractions had greater LOI due to presence of hydroxide and carbonate species. Chemical composition was found to vary modestly depending on particle size, while pH only varied for the coarsest fraction, and reactivity and leaching were similar for all fractions. Higher CO <sub>2</sub> uptake was achieved with smaller particle size and this was attributed to increased surface area (assumed).
De et al. [32]	It is not mentioned how the reported particle size of the slag, 83–90 μm, was determined nor how this size fraction was obtained.	Particle size is only reported, with no further discussion.
Blackbitch et al. [28]	The LAF slag was milled in a corundum ball mill to a particle size below 150 μm; the method of classification is not specified.	Previous studies are also mentioned, but there is no discussion regarding particle size.
Argon Oxygen Decarburization (AOD)	The AOD slag, as received, was sieved to a particle size <150 μm, with 90% of the slag passing this mesh size. This study also used the same slag samples (SS and LAF) that were prepared by Blackbitch et al. [28] and by Blackbitch et al. [24].	Particle size was related to the elemental composition (theory relates to different stages and fractions, and to their relative contribution, which was higher in the finer materials. Greater CO <sub>2</sub> uptake was observed for finer SS slag fractions, and it was concluded that the finer the slag, the greater the CO <sub>2</sub> uptake. Maximum calcium conversion was related to the finest size fraction, but not to the finest fraction.
Cheng et al. [28]	It is not mentioned how the reported particle size of the slag, 44 μm, was determined nor how this size fraction was obtained. SEM imaging was used, post-carbonation, to visualize particle size and shape.	Similar comments to those made by Cheng et al. [28,31] regarding SEM images are made. A comparative table shows particle size of other studies, but no discussion about particle size is made.
Cripps et al. [37]	The slag was crushed to a final particle size below 4 mm; the method of size classification is not mentioned.	Low carbonation conversion was associated to the coarse particle size used and, in turn, the low surface area of the slag, which is concluded to not favor the distribution kinetics of reactive species. It is suggested that a pre-treatment stage based on particle size reduction could contribute to an optimized process.

How characterization of particle size distribution pre- and post-reaction provides mechanistic insights into mineral carbonation. [Geosciences, \(2018\), 8\(7\), 260.](#)

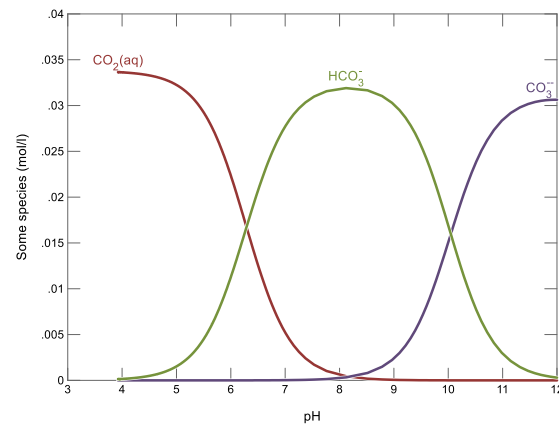
# Reactor Design: conventional vs. intensified/integrated



# Geochemical Modeling: P & T effects



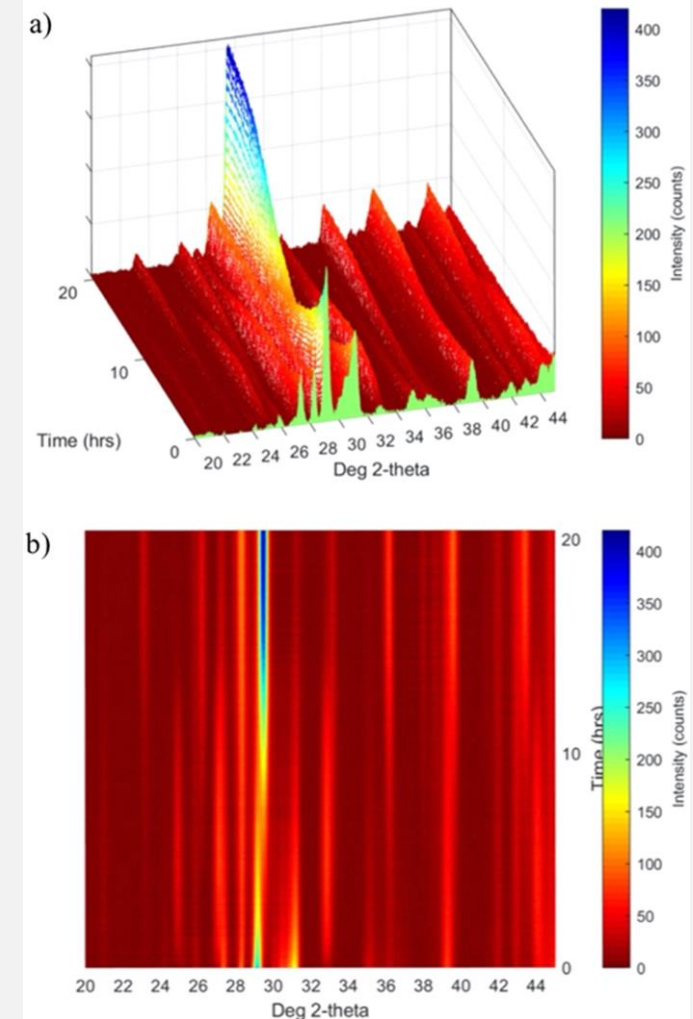
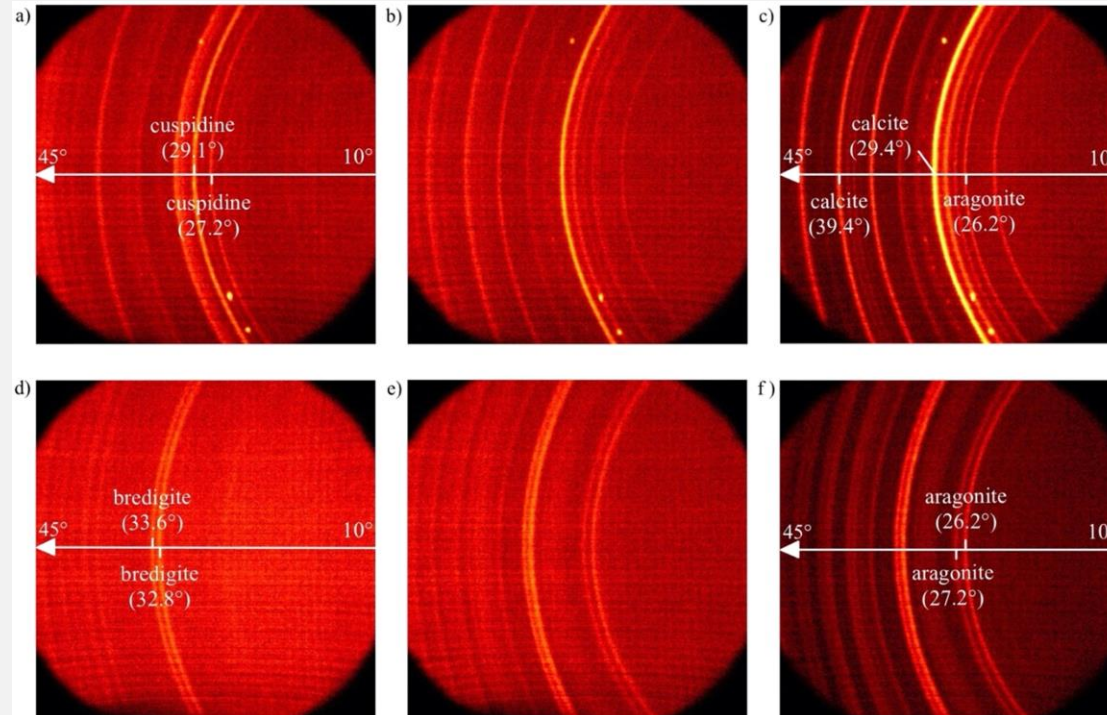
T = 150°C, P = 60 bar  $\text{CO}_2$ , 0.64 M NaCl



T = 25°C, P = 1 bar  $\text{CO}_2$



# In-situ Investigation



UNIVERSITY  
of GUELPH

Pressurized in situ x-ray diffraction insights into super/subcritical carbonation reaction pathways of steelmaking slags and constituent silicate minerals, [The Journal of Supercritical Fluids, \(2021\), 171, 105191](#).

**Thank You.**

**Questions?**

**santosr@uoguelph.ca**

**UNIVERSITY  
of GUELPH**

**IMPROVE LIFE.**